Libr

UNIVERSITY OF PENNSYLVANIA

SOME THERMODYNAMIC PROPERTIES OF LITHIUM HYDROXIDE AND THE DISSOCIATION OF WATER IN LITHIUM CHLORIDE SOLUTIONS.

FRANK EVANS SWINDELLS

A THESIS
IN CHEMISTRY
PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

PHILADELPHIA
1925

STANFORD UNIVERSITY LIBRARIES

3781
P41S
UNCLASSED

SOME THERMODYNAMIC PROPERTIES OF LITHIUM HYDROXIDE AND THE DISSOCIATION OF WATER IN LITHIUM CHLORIDE SOLUTIONS.

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL OF THE UNIVERSITY OF PENNSYLVANIA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

FRANK EVANS SWINDELLS

PHILADELPHIA

1925

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Herbert S. Harned, under whose direction this investigation was carried out, and to Dr. Walter W. Lucasse and Mr. Gösta Åkerlöf, who rendered valuable assistance in taking the readings.

SOME THERMODYNAMIC PROPERTIES OF LITHIUM HYDROXIDE, AND THE DISSOCIATION OF WATER IN LITHIUM CHLORIDE SOLUTIONS

I. INTRODUCTION

This investigation comprises the evaluation of the activity coefficients of lithium hydroxide in aqueous solution, and in solutions of lithium chloride of varying strength; the extension of the data of previous investigators on the activity coefficients of hydrochloric acid in lithium chloride solutions; and an attempt to calculate the ionic product of water in lithium chloride solutions.

II. PREPARATION OF MATERIALS, ETC.

Lithium amalgam.—The mercury used was purified by repeatedly passing it in the form of a fine spray through a long column of a solution of mercurous nitrate and nitric acid, and then distilling it four times in vacuo. The amalgam was prepared electrolytically from this mercury by making it the cathode in the electrolysis of lithium chloride, using as anode a graphite rod, separated from the rest of the cell by a porous cup. At the conclusion of the electrolysis the malgam was drawn through a capillary tube into a highly evacuated glass bulb, to which was sealed a capillary tube and stopcock. The bulb was then sealed off from the vacuum line and inverted, so that the capillary used for the admission and withdrawal of the amalgam was now at the bottom. After standing for several days, to permit a thorough drying, and all insoluble impurities to rise to the surface, it was diluted to the desired strength by allowing it to flow through the capillary into a larger evacuated vessel of similar form containing mercury, which was then sealed off and inverted. From this vessel the amalgam was transferred directly to the reservoir of the electrode without coming in contact with the air.

Lithium Hydroxide.—This was prepared by mixing nearly equivalent amounts of hot, nearly saturated solutions of barium hydroxide and lithium sulfate, so that a trace of the former remained in excess. After standing for several days, the clear supernatent liquid was decanted from the precipitate. In this way a solution free from carbonate was prepared. It contained traces of dissolved barium hydroxide and sulfate, which were not believed to be detrimental to the accuracy of the results. A stronger solution was prepared by dissolving the lithium hydroxide of commerce in water, adding barium hydroxide in slight excess, and decanting as before. These solutions, which were about 0.5 and 4 molal, respectively, were preserved in bottles fitted with siphons and protected from the carbon dioxide of the air by soda-lime tubes. They were analysed by titrating weighed portions with hydrochloric acid which had been standardized gravimetrically. The solutions used in the cells were prepared by diluting weighed amounts of the above with redistilled water. Since dissolved air is not permissible with the use of an alkali amalgam electrode, the solutions were boiled in vacuo and introduced into the cells without coming in contact with the air. Correction was made for the water boiled off.

Lithium Chloride.—A solution of the pure salt was prepared and analysed, by treating a weighed portion with a little nitric acid and an excess of silver nitrate, and weighing the silver chloride precipitated. As a check, another portion was treated with an excess of sulfuric acid and evaporated to dryness and heated to fusion in a platinum dish, and the lithium sulfate weighed. Excellent agreement with the other method of analysis was obtained.

The alkali solutions containing lithium chloride were prepared by mixing weighed amounts of the analysed solutions of lithium hydroxide and lithium chloride with a little more than enough water to bring them to the desired strength. They were then boiled in vacuo in weighed flasks, correction being made for the water boiled off. They were then transferred to the cells without coming in contact with the air.

Hydrochloric Acid.—The "C. P" acid was diluted to about 20 per cent by weight and distilled. Stock solutions were prepared

by dilution of this acid, and analysed by precipitating silver chloride from weighed portions. The acid solutions containing lithium chloride were made by mixing weighed amounts of the above solutions with analysed lithium chloride solutions and diluting with enough water to bring them to the required concentrations.

Hydrogen.—A solution of sodium hydroxide was electrolysed, using a platinum anode and nickel cathode, in a cell designed to prevent mixing of the hydrogen evolved. The hydrogen was passed through alkaline pyrogallol, and a saturator immersed in the thermostat containing a solution of approximately the same composition as that in the cell, and then conducted to the hydrogen electrode.

All measurements were made in a thermostat, electrically and controlled to a temperature of 25° ± 0.05° C. The electromotive force measurements were made on a Leeds and Northrup Type K potentiometer. The battery of Weston cells used as a standard was compared from time to time against one recently certified by the maker.

III. THE ACTIVITY COEFFICIENT OF LITHIUM HYDROXIDE IN AQUEOUS SOLUTION

The method used is essentially that used by Knobel[1] and Harned[2], who measured the activities of sodium and potassium hyroxides, respectively. It involves measurement of the electromotive force developed in the following concentration cell without liquid junction:

$$H_2 \mid LiOH_{m1} \mid Li_xHg \mid LiOH_{m2} \mid H_2$$

where m_1 and m_2 are different concentrations of lithium hydroxide. From the data so obtained, the values of the activity coefficient at various concentrations are calculated by the application of thermodynamic principles.

---

[1] Knobel, *J. Am. Chem. Soc.*, **45**, 70 (1923).
[2] Harned, *J. Am. Chem. Soc.*, **47**, 676 (1925).

Flowing alkali amalgam electrodes have been studied by Meyer,[3] and later by Lewis and his associates,[4] who found them to be among the most reproducible metallic electrodes. They have been successfully applied to the measurement of the activity coefficients of strong electrolytes in concentration cells by a number of investigators.[5]

The cell used was essentially the same as that used by Knobel,[6] except that the electrolyte remained stationary during the measurement. The cell proper consisted of two symmetrical parts, each containing one of the two solutions to be measured. Each part was H-shaped; one limb of each contained a hydrogen electrode prepared in the usual way, and into the others dipped the two exit tubes of the amalgam electrode. The latter consisted of a reservoir filled in vacuo with about 30 c. cm. of amalgam. Two capillary tubes with stopcocks led from this reservoir into the two parts of the cell, thus permitting the amalgam to be run into the two solutions simultaneously. These tubes were of such size and shape that the amalgam flowed in a solid stream from each tip for a distance of about one centimeter, where it broke into a spray of small globules. The rate of flow was about three cubic centimeters per minute for each tip. From the bottom of the amalgam electrode compartments tubes with stopcocks led into a large flask resting on the bottom of the thermostat. To this flask was also attached a line leading to a vacuum pump.

After cleaning and drying, the cell was set up in the thermostat and evacuated to about 0.1 mm. pressure. The flasks containing the solutions to be measured, boiled in vacuo, were then attached to tubes leading into the two parts of the cell, and the solutions then allowed to run in and fill the cell completely. Hydrogen was then conducted through the hydrogen

---

[3] Meyer, *Z. physik. Chem.*, **7**, 477 (1891).

[4] Lewis and Kraus, *J. Am. Chem. Soc.*, **32**, 1459 (1910). Lewis and Keyes, *ibid.*, **34**, 119 (1912); **35**, 340 (1913). Lewis and Argo, *ibid.*, **37**, 1983 (1915).

[5] MacInnes and Parker, *J. Am. Chem. Soc.*, **37**, 1445 (1915). Pearce and Mortimer, *ibid.*, **40**, 509 (1918). Allmand and Pollack, *J. Chem. Soc.*, **115**, 1020 (1919). Ming Chow, *J. Am. Chem. Soc.*, **42**, 488 (1920). MacInnes and Beattie, *ibid.*, **42**, 1117 (1920). Knobel, *ibid.*, **45**, 70 (1923). Harned, *ibid.*, **47**, 676, 684, 689 (1925).

[6] Knobel, *J. Am. Chem. Soc.*, **45**, 70 (1923). See also Harned, *ibid.*, **47**, 676 (1925).

electrode compartments for about three hours, after which the amalgam was allowed to flow through the cell, the excess being removed through the exit tubes at the bottom in such a manner that the liquid level in the hydrogen electrode compartments remained constant. While the amalgam was flowing, readings of the electromotive force developed between the two hydrogen electrodes were taken continuously, and their mean taken as the electromotive force of the cell.

The results are shown inTable I. The first two columns show the concentrations of the two solutions contained in the cell, expressed in formula weights (23.95 grams) per 1000 grams of water. The third column contains the electromotive forces observed. The ratio of the activity coefficients in the two solutions is given by the following equation, relating the activities, concentration, and electromotive force:

$$\log \frac{\gamma_2}{\gamma_1} = -\frac{E}{0.1183} - \log \frac{m_2}{m_1} - \tfrac{1}{2} \log \frac{a_{H_2O(1)}}{a_{H_2O(2)}}\,,^{7} \quad \ldots\ldots\ldots\ldots (1)$$

The activity of the water in the solutions was calculated by the method proposed by Lewis and Randall.[8] Approximate values

---

[7] The reactions taking place in the two parts of the cell are

$$Li + H_2O(2) = \tfrac{1}{2}\, H_2 + Li^+(2) + OH^-(2) \text{ and}$$
$$\tfrac{1}{2}\, H_2 + Li^+(1) + OH^-(1) = Li + H_2O(1).$$

Taking the sum, we obtain for the total cell reaction

$$Li^+(1) + OH^-(1) + H_2O(2) = Li^+(2) + OH^-(2) + H_2O(1).$$

The thermodynamic equation for such a concentration cell relating the electromotive force and the activities of the various ionic species involved is

$$E = \frac{RT}{nF} \ln \frac{a^+_{Li(2)}\; a^-_{OH(2)}\; a_{H_2O}}{a^+_{Li(2)}\; a^-_{OH(1)}\; a_{H_2O}}$$

If we substitute for $a^+_{Li}\; a^-_{OH}, \gamma^2 m^2$, where γ is the activity coefficient, and for the constants their numerical values we get

$$E = 0.05915 \log \frac{\gamma_2^{\,2} m_2^{\,2}\; a_{H_2O(1)}}{\gamma_1^{\,2} m_1^{\,2}\; a_{H_2O(2)}}$$

which upon rearrangement reduces to (1) above.

[8] Lewis and Randall, "Thermodynamics," p. 269, *McGraw Hill Book Co.* (1923).

of the activity of lithium hydroxide were computed, assuming that the activity of the water is the same in the two solutions. These values are then used for the graphical evaluation of the activity of the water for each concentration of lithium hydroxide. These values are given in the fourth column, and in the fifth the values of $\frac{\gamma_2}{\gamma_1}$ computed by equation (1). The last column contains the absolute values of the activity coefficients of lithium hydroxide at m_2 concentration, calculated on the assumption that the activity co-efficient of 0.01 molal lithium hydroxide is 0.920, the same value adopted by Knobel[9] for potassium hydroxide and by Harned[10] for sodium hydroxide. This value is subject to revision at a later date when more data are available for dilute solutions.

---

[9] Knobel, *J. Am. Chem. Soc.*, **45**, 70 (1923).
[10] Harned, *ibid.*, **47**, 680 (1925).

TABLE I

ACTIVITY COEFFICIENTS OF LITHIUM HYDROXIDE

m_2	m_1	E	$\frac{a_{H_2O(2)}}{a_{H_2O(1)}}$	$\frac{\gamma_2}{\gamma_1}$	γ_2
0.0505	0.01006	0.0761	0.999	0.877	0.806
0.1008	0.01005	0.1088	0.998	0.828	0.761
0.1038	0.01030	0.1084	0.998	0.817	0.750
0.0235	0.0978	−0.0669	1.000	1.131	0.858
0.242	0.1013	0.0396	0.996	0.904	0.683
0.346	0.0993	0.0566	0.995	0.863	0.653
0.432	0.0993	0.0664	0.992	0.833	0.631
0.553	0.1006	0.0765	0.990	0.798	0.603
0.611	0.1011	0.0808	0.989	0.791	0.599
1.063	0.1006	0.1069	0.981	0.748	0.565
1.812	0.0997	0.1307	0.966	0.687	0.520
2.386	0.1043	0.1412	0.956	0.668	0.503
2.577	0.1051	0.1438	0.952	0.654	0.493
3.926	0.1051	0.1651	0.930	0.632	0.482

IV. THE ACTIVITY COEFFICIENT OF LITHIUM HYDROXIDE IN LITHIUM CHLORIDE SOLUTIONS

Measurements were made of the following cell:

$$H_2 \left| LiOH_{m1} \right| Li_xHg \left| \begin{matrix} LiOH_{m2} \\ LiCl_m \end{matrix} \right| H_2$$

where m_1 and m_2 have approximately the same value, and the value of m is varied. The apparatus and the method of procedure were the same as described in the preceding section. Table 2 shows the results obtained. Since the solutions had to be boiled, it was not convenient to make m_1 and m_2 exactly the desired value, and hence a correction to the electromotive force observed was necessary. This correction, made on the assumption that over the small range the activity coefficients were constant, is shown in the fifth column of the table. The equation used is as follows:

$$\Delta E = 0.1183 \log \frac{m_1}{m_0} - 0.05915 \frac{m_2(m_2+m)}{m_0(m_0+m)} \quad \ldots\ldots\ldots (2)$$

in which m_0 is the desired concentration (0.1 or 0.01) and ΔE the correction to be applied to the observed electromotive force. It is again necessary to evaluate the activity of the water in the solution. This is done on the assumption that the activity of water in the solution is the same as if the total concentration were lithium chloride. An equation has been derived by Harned[1] by which the vapor pressure, and hence the activity ratio of a salt solution may be calculated from constants derived from the activity of the solute:

$$\ln \frac{p_0}{p} = \frac{c}{55.5}\left(2 + 2.303\alpha c - \frac{4.606\ \beta\alpha'}{\alpha'+1} c^{\alpha'}\right) \quad \ldots\ldots (3)$$

[1] Harned, *J. Am. Chem. Soc.*, **42**, 1808 (1920); **44**, 252 (1922).

The value of the constants based on the determination of the activity of lithium chloride by MacInnes and Beattie[2] are as follows:

$$\alpha = 0.21 \qquad \beta = 0.323 \qquad \alpha' = 0.463$$

The values thus calculated are shown in the sixth column, and in the last column are given the activity coefficients, calculated from the following equation:

$$\log \frac{\gamma}{\gamma_0} = \frac{E}{0.1183} - \log \frac{\sqrt{m_0(m+m_0)}}{m_0} - \tfrac{1}{2} \log \frac{a_{H_2O(1)}{}^3}{a_{H_2O(2)}} \qquad (4)$$

[2] MacInnes and Beattie, *J. Am. Chem. Soc.*, **42**, 1117 (1920).

[3] The derivation of this equation is exactly analogous to that of equation (1).

Table II

Activity Coefficients of Lithium Hydroxide in Lithium Chloride

$m_0 = 0.01$ $\gamma^0 = 0.920$

m_1	m_2	m	E	ΔE	E_{cor}	$\frac{a_{H_2O(2)}}{a_{H_2O(1)}}$	γ
0.00996	0.01001	0.01216	0.01729	−0.00025	0.0170	1.000	0.861
0.01001	0.01005	0.0550	0.03921	−0.00019	0.0391	0.998	0.772
0.01001	0.01009	0.1825	0.06116	−0.00020	0.0609	0.994	0.684
0.01001	0.01003	0.276	0.06900	−0.00001	0.0690	0.990	0.655
0.01001	0.00995	0.390	0.07654	0.00016	0.0767	0.987	0.643
0.00997	0.01002	0.635	0.08645	−0.00017	0.0863	0.978	0.607
0.01002	0.00999	1.044	0.09622	0.00028	0.0965	0.962	0.575
0.01004	0.01002	2.17	0.11274	0.00016	0.1127	0.911	0.533
0.01005	0.01002	4.15	0.13194	0.00014	0.1321	0.793	0.526
0.00998	0.01005	8.36	0.16250	−0.00021	0.1624	0.486	0.524

$m_0 = 0.1$ $\gamma_0 = 0.755$

m_1	m_2	m	E	ΔE	E_{cor}	$\frac{a_{H_2O(2)}}{a_{H_2O(1)}}$	γ
0.1003	0.0993	0.0175	0.00284	0.00049	0.0033	1.000	0.743
0.0988	0.0998	0.0916	0.01388	−0.00054	0.0133	0.997	0.706
0.1003	0.1000	0.1941	0.02218	0.00015	0.0223	0.994	0.678
0.1003	0.0985	0.2109	0.02307	0.00067	0.0237	0.993	0.677
0.1003	0.1008	0.222	0.02432	−0.00009	0.0242	0.993	0.671
0.1003	0.1000	0.456	0.03571	0.00018	0.0359	0.984	0.639
0.1003	0.0993	0.469	0.03588	0.00039	0.0363	0.984	0.636
0.0997	0.1012	0.746	0.04537	−0.00020	0.0447	0.974	0.611
0.1003	0.0984	0.978	0.04942	0.00060	0.0500	0.964	0.598
0.1003	0.1000	1.208	0.05467	0.00013	0.0548	0.955	0.592
0.0999	0.1001	2.85	0.07632	0.00009	0.0762	0.872	0.572
0.1003	0.1047	2.95	0.07831	−0.00109	0.0772	0.866	0.572
0.0999	0.1000	4.84	0.09577	−0.00007	0.0957	0.741	0.589
0.0999	0.1038	8.48	0.12706	−0.00102	0.1260	0.472	0.651

V. THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN LITHIUM CHLORIDE SOLUTIONS

Harned[1] has measured the electromotive force developed in the cells

$$H_2 \left| \begin{matrix} HCl_{m_0} \\ LiCl_m \end{matrix} \right| HgCl \left| Hg \right.$$

in which m_0 is constant at 0.1 molal and m varied from zero to about four molal. From the results thus obtained he calculated the activity coefficient of hydrochloric acid in the salt solutions.[2]

In the present investigation a similar series of measurements of the cells

$$H_2 \left| \begin{matrix} HCl_{m_0} \\ LiCl_m \end{matrix} \right| AgCl \left| Ag \right.$$

have been made, in which m_0 has the values 0.1 and 0.01 molal and m is varied from zero to about four molal.

The cell used was of the H-shaped type commonly used in this kind of measurement. The silver-silver chloride electrodes were prepared according to the technique of Noyes and Ellis,[3] and the hydrogen electrodes in the usual manner. The results are shown in Table III. The first column shows the concentration of the lithium chloride, the second the observed electromotive force, the third the barometric pressure, and the fourth column gives the values of the electromotive force corrected to 760 mm partial pressure of hydrogen. The fifth column contains the electromotive force of the hypothetical cells

$$H_2 \left| HCl_{m_0} \right| AgCl \left| Ag \right| AgCl \left| \begin{matrix} HCl_{m_0} \\ LiCl_m \end{matrix} \right| H_2$$

obtained by subtracting the observed electromotive force from that of the cell

---

[1] Harned, *J. Am. Chem. Soc.*, **42**, 1808 (1920).
[2] Harned and Brumbaugh, *J. Am. Chem. Soc.*, **44** 2729 (1922).
[3] Noyes and Ellis, *J. Am. Chem. Soc.*, **39**, 2245 (1917).

$$H_2 \mid HCl_{m0} \mid AgCl \mid Ag$$

The last column contains activity co-efficients calculated from the equation

$$\log \frac{\gamma}{\gamma_0} = \frac{E_0 - E_{cor}}{0.1183} - \log \frac{\sqrt{m_0(m+m_0)}}{m_0} \quad \ldots\ldots\ldots (5)$$

The values of γ_0 are taken from Lewis'[4] calculation of the measurements of Linhart[5] and of Noyes and Ellis.[5]

The activity coefficients of the 0.1 M series are in good agreement with those obtained by Harned, below a concentration of 1 M, but above this point the divergence becomes appreciable and at the highest concentration corresponds to a difference of more than a millivolt.

---

[4] Lewis and Randall, "Thermodynamics," p. 336, *McGraw Hill Book Co.* (1923).
[5] Linhart, *J. Am. Chem. Soc.*, **41**, 1175 (1919).

TABLE III

ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN LITHIUM CHLORIDE

$m_0 = 0.01$ $\gamma_0 = 0.924$

m	E_{obs}	Bar.	E_{cor}	$E_0 - E_{cor.}$	γ
0.00000	0.46427	771.0	0.46449	0.0000	0.924
0.00767	0.45138	771.0	0.45160	0.0129	0.893
0.01028	0.44825	769.1	0.44849	0.0160	0.886
0.01944	0.44005	764.8	0.44036	0.0241	0.862
0.0422	0.42655	769.1	0.42679	0.0377	0.842
0.0727	0.41644	764.9	0.41675	0.0477	0.814
0.1209	0.40605	769.2	0.40629	0.0582	0.792
0.1989	0.39496	764.9	0.39527	0.0692	0.778
0.4024	0.37830	769.2	0.37854	0.0860	0.767
0.699	0.36314	764.8	0.36337	0.1011	0.786
1.004	0.35142	765.5	0.35172	0.1128	0.824
2.189	0.31776	770.4	0.31798	0.1465	1.080
3.987	0.27538	770.4	0.27560	0.1889	1.826

$m_0 = 0.1$ $\gamma_0 = 0.814$

m	E_{obs}	Bar.	E_{cor}	$E_0 - E_{cor}$	γ
0.0000	0.35225	760.0	0.35265	0.0000	0.814
0.0705	0.34031	759.9	0.34070	0.0120	0.787
0.1101	0.33498	759.9	0.33532	0.0173	0.786
0.2004	0.32666	759.9	0.32706	0.0256	0.772
0.3693	0.31507	761.0	0.31547	0.0372	0.775
0.704	0.29992	770.6	0.30014	0.0525	0.796
1.007	0.28881	770.6	0.28901	0.0636	0.844
2.198	0.25494	764.8	0.25526	0.0974	1.131
3.695	0.22034	764.8	0.22066	0.1320	1.725

VI. THE ACTIVITY COEFFICIENT AND DISSOCIATION OF WATER IN LITHIUM CHLORIDE SOLUTION

The results of the measurements of the preceding cells, together with other data obtainable from the literature, permit the calculation of the activity coefficient and ionic concentration product of water in lithium chloride solutions, by a method analogous to that used by Harned for sodium and potassium chloride solutions.[1]

The electromotive force of the cell

$$H_2 \left| HCl_{m_0} \right| AgCl \left| Ag \right| AgCl \left| \begin{matrix} HCl_{m_0} \\ LiCl_m \end{matrix} \right| H_2$$

which will be designated as E_1, is related to the activity coefficients and concentrations of the ionic species by the following equations:

$$E_1 = 0.05915 \log \frac{\gamma_{H(s)}\ \gamma_{Cl(s)}\ (m+m_0)m_0}{\gamma_{H(m_0)}\ \gamma_{Cl(m_0)}\ m_0^2} \quad \ldots\ldots\ldots (6)$$

For the cell

$$H_2 \left| LiOH_{m_0} \right| Li_xHg \left| \begin{matrix} LiOH_{m_0} \\ LiCl_m \end{matrix} \right| H_2$$

$$E_2 = 0.05915 \log \frac{\gamma_{Li(s)}\ \gamma_{OH(s)}\ a_{H_2O(m_0)}\ (m+m_0)m_0}{\gamma_{Li(m_0)}\ \gamma_{OH(m_0)}\ a_{H_2O(s)}\ m_0^2} \quad \ldots\ldots (7)$$

Similarly for the cell

$$Ag \mid AgCl \mid LiCl_{(m_0)} \mid Li_xHg \mid LiCl_{(m_0+m)} \mid AgCl \mid Ag$$

$$E_3 = 0.05915 \log \frac{\gamma_{Li(m+m_0)}\ \gamma_{Cl(m+m_0)}\ (m+m_0)^2}{\gamma_{Li(m_0)}\ \gamma_{Cl(m_0)}\ m_0^2} \quad \ldots\ldots\ldots (8)$$

[1] Harned, *J. Am. Chem. Soc.*, **47**, 930 (1925).

If the sum of (6) and (7) be subtracted from (8) and the terms rearranged the following expression is obtained:[2]

$$E_1 + E_2 - E_3 = 0.05915 \log \frac{\frac{\gamma_{H(s)}\ \gamma_{OH(s)}}{a_{H_2O(s)}}}{\frac{\gamma_{Hm_0}\ \gamma_{OHm_0}}{a_{HO_2m_0}}} = 0.05915 \log \frac{K_{\gamma(s)}}{K_{\gamma(m_0)}} \quad (9)$$

The calculation is shown in Table IV. The values of E_1 are obtained by interpolation fromTable III, and the values of E_2 from Table II. For the calculation of E_3 activity coefficients based on the determinations of MacInnes and Beattie[3] were used. In order to calculate $K\gamma$ for the salt solutions it is necessary to determine its value at 0.01 molal concentration by an independent method. From the work of Lewis and Sargent and others[4] it seems probable that in dilute solutions of mixtures the activity coefficient of one constituent of the mixture depends only on the total concentration. We shall therefore assume that the activity coefficient of water is a function of the sum of the concentrations of the lithium chloride and water, and since the latter is negligible in comparison with the former, a function of the concentration of the lithium chloride.[5]

From the theory of DeBye and Hückel[6] it follows that as the concentration approaches zero the activity coefficient becomes the following function of the concentration:

$$\log \gamma = -\beta m^{\frac{1}{2}} \quad (10)$$

[2] This procedure involves the assumption that the activity coefficient of the lithium ion has the same value in a solution of lithium chloride as in a solution of lithium chloride and lithium hydroxide having the same total concentration, and a similar assumption in regard to the chloride ion in lithium chloride and lithium chloride and hydrochloric acid of the same total concentration. The accuracy of this assumption is measured by the extent to which the values of $K\gamma$ calculated from different values of m_0 agree at the same total concentration. For this reason calculation of two series of values were made, in which m_0 had the values 0.1 and 0.01.

[3] MacInnes and Beattie, *J. Am. Chem. Soc.*, **42**, 1117 (1920). Lewis and Randall, "Thermodynamics," p. 362. *McGraw Hill Book Co.* (1923).

[4] Lewis and Sargent, *J. Am. Chem. Soc.*, **31**, 335 (1909). Harned, *ibid.*, **38**, 1986 (1916). Linhart, *ibid.*, **38**, 2356 (1916). Loomis, Essex and Meacham, *ibid.*, **39**, 1133 (1917).

[5] It is understood that by the concentration of water is meant the concentration of that portion of the water which acts as an electrolyte, *i. e.*, the concentration of the ionized water.

[6] DeBye and Hückel, *Physik. Z.*, **9**, 185 (1923).

where for uniunivalent electrolytes β has a value of approximately 0.5. It has been shown[7] that at 0.01 M this equation gives a value of γ which is lower than observed values. A value of 0.42 is assumed for β which gives $\gamma_{H_2O}=0.908$ and $K\gamma=0.824$ at 0.01 molal concentration. The values of $K\gamma$ shown in the fifth column are calculated on the basis of these assumptions.

The activity coefficient of water in the salt solution, denoted by $\gamma(s)$, is next calculated. Since

$$\gamma_{(s)}=\sqrt{\gamma_{OH}\gamma_H}=\sqrt{K\gamma a_{H_2O(s)}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

it is necessary to evaluate $a_{H_2O(s)}$. For this purpose equation (3) is again employed, giving the values shown in the sixth column.

The results obtained also permit the calculation of the ionic concentration product of water in the lithium chloride solutions. For the reaction

$$H_2O=H^+ + OH^-$$

the dissociation constant is so defined that

$$K_w=\frac{a_H a_{OH}}{a_{H_2O}}=\frac{\gamma_H\gamma_{OH}}{a_{H_2O}}m_w^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (12)$$

where K_w is the dissociation constant and m_w the concentration of the hydrogen or hydroxyl ions of water. If this be solved for m_w an expression is obtained which permits the calculation of m_w from the data at hand:

$$m_H=m_{OH}=m_w=\frac{\sqrt{K_w a_{H_2O}}}{\gamma_H\ \gamma_{OH}}=\frac{\sqrt{K_w}}{K\gamma} \quad \ldots\ldots\ldots\ldots (13)$$

The value of K_w used is that calculated from electrode potentials by Lewis and Randall, 1.005×10^{-8}.

---

[7] Randall and Vanselow, *J. Am. Chem. Soc.*, **46**, 2418 (1924).

[8] Lewis and Randall, "Thermodynamics," p. 434. *McGraw Hill Book Co.* (1923).

TABLE IV

$m_0 = 0.01$

$m_0 + m$	E_1	E_2	E_3	$E_1 + E_2 - E_3$	$K\gamma$	a_{H_2O}	γ_s	$m_w \times 10^7$
0.01	0.0000	0.0000	0.0000	0.0000	0.824	1.000	0.908	1.104
0.02	0.0158	0.0149	0.0338	−0.0031	0.730	0.999	0.855	1.173
0.03	0.0246	0.0234	0.0531	−0.0051	0.676	0.999	0.821	1.220
0.05	0.0367	0.0339	0.0781	−0.0075	0.615	0.999	0.784	1.277
0.1	0.0521	0.0478	0.1113	−0.0114	0.528	0.996	0.726	1.379
0.2	0.0682	0.0618	0.1449	−0.0149	0.461	0.993	0.677	1.476
0.3	0.0777	0.0704	0.1643	−0.0162	0.439	0.990	0.659	1.514
0.5	0.0909	0.0811	0.1906	−0.0186	0.399	0.983	0.627	1.588
0.75	0.1027	0.0895	0.2122	−0.0200	0.378	0.974	0.607	1.632
1.0	0.1123	0.0955	0.2277	−0.0199	0.380	0.964	0.605	1.630
2.0	0.1425	0.1108	0.2730	−0.0197	0.383	0.920	0.593	1.620
3.0	0.1665	0.1216	0.3066	−0.0185	0.401	0.866	0.589	1.582

$m_0 = 0.1$

$m_0 + m$	E_1	E_2	E_3	$E_1 + E_2 - E_3$	$K\gamma$	a_{H_2O}	γ_s	$m_w \times 10^7$
0.1	0.0000	0.0000	0.0000	0.0000	0.528	0.996	0.726	1.379
0.2	0.0161	0.0142	0.0336	−0.0033	0.465	0.993	0.680	1.470
0.4	0.0329	0.0289	0.0680	−0.0062	0.415	0.986	0.640	1.555
0.6	0.0440	0.0374	0.0890	−0.0076	0.393	0.979	0.621	1.600
0.8	0.0524	0.0435	0.1045	−0.0086	0.378	0.972	0.606	1.630
1.1	0.0634	0.0505	0.1221	−0.0082	0.384	0.960	0.607	1.617
2.1	0.0924	0.0667	0.1653	−0.0062	0.415	0.915	0.616	1.556
3.1	0.1163	0.0777	0.1980	−0.0040	0.452	0.860	0.623	1.492

VII. DISCUSSION

In Fig. 1 the activity co-efficients of lithium hydroxide in pure water and in lithium chloride solutions are plotted against the total concentration. It is of interest to note that no minimum could be detected in the activity coefficient of aqueous lithium hydroxide up to nearly 4 M, nor for the 0.01 series up to above 8 M. Comparison of the activity coefficients of the three alkali hydroxides shows that for a given concentration the activities increase with increase in atomic weight, whereas for simple salts such as the chlorides the converse is true. It should be emphasized that in the calculation of these results a value was assumed for the activity coefficient of 0.01 M lithium hydroxide which has little basis of experimental fact, but when such evidence is obtained revision of the calculation will be a simple matter. A more important source of error is the inaccuracy of the amalgam electrodes in the most dilute solutions.[1] In the pure hydroxide series most of the measurements were made with the comparison solution about 0.1 M, so that the relative value of the results is not affected by this source of error.

In Fig. 3 the results of the calculation of the activity coefficient and ionic concentration of water are shown. It will be noted that the value selected for the value of the activity coefficient of water in 0.01 M lithium chloride was based on the assumption that this quantity is the same function of the concentration as for strong electrolytes. No data are at present available to test this assumption. However, this uncertainty does not influence the relative values of the results, but only their absolute values. A similar statement may be made in regard to the value of the ionization constant of water, which is based on a calculation involving the estimation of liquid junction potentials and absolute values of activity coefficients which may be in error.

Aside from these, the principal assumptions in these calculations are that the chloride ion has the same activity in hydrochloric acid and lithium chloride as in pure lithium chloride of the same ionic strength, and that the lithium ion has the same

[1] For a discussion of this point see Lewis and Randall, *J. Am. Chem. Soc.*, **43**, 1112 (1921).

activity in a solution of lithium hydroxide and lithium chloride as in lithium chloride of the same ionic strength. That these assumptions are probably valid at least up to 1 M, is shown by the coincidence of the curves of the 0.1 M and 0.01 M series. Above this value the departure may be accounted for by the experimental error in the acid series, which is probably rather large, due to the solubility of silver chloride in strong lithium chloride solutions, or more likely to errors in the akali series, where the experimental difficulties become great in concentrated solutions, due to more rapid decomposition of the amalgam.

VIII. SUMMARY

1. Measurements of the following types of cells were made:

$$H_2 \mid LiOH_{m_1} \mid Li_xHg \mid LiOH_{m_2} \mid H_2$$

$$H_2 \left| \begin{matrix} LiOH_{m_0} \\ \end{matrix} \right| \begin{matrix} Li_xHg \\ \end{matrix} \left| \begin{matrix} LiOH_{m_0} \\ LiCl_m \end{matrix} \right| H_2$$

$$H_2 \left| \begin{matrix} HCl_{m_0} \\ LiCl_m \end{matrix} \right| \begin{matrix} AgCl \\ \end{matrix} \left| \begin{matrix} Ag \\ \end{matrix} \right.$$

2. From the results so obtained the activity coefficients of lithium hydroxide in aqueous solution and in lithium chloride solutions of varying strength, and of hydrochloric acid in lithium chloride solutions were calculated.

3. A calculation of the activity coefficient and the ionic concentration product of water in lithium chloride solutions was made.

4. The assumptions involved and other sources of error were discussed.

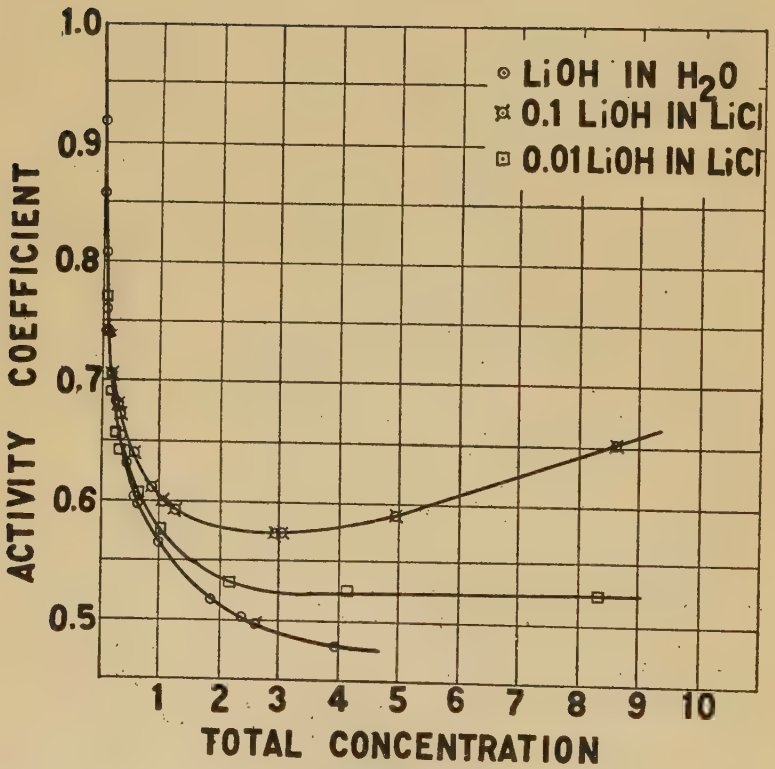
1.0
0.9
0.8
0.7
0.6
0.5
ACTIVITY COEFFICIENT
1 2 3 4 5 6 7 8 9 10
TOTAL CONCENTRATION
LiOH IN H2O
0.1 LiOH IN LiCl
0.01 LiOH IN LiCl

FIG. 1

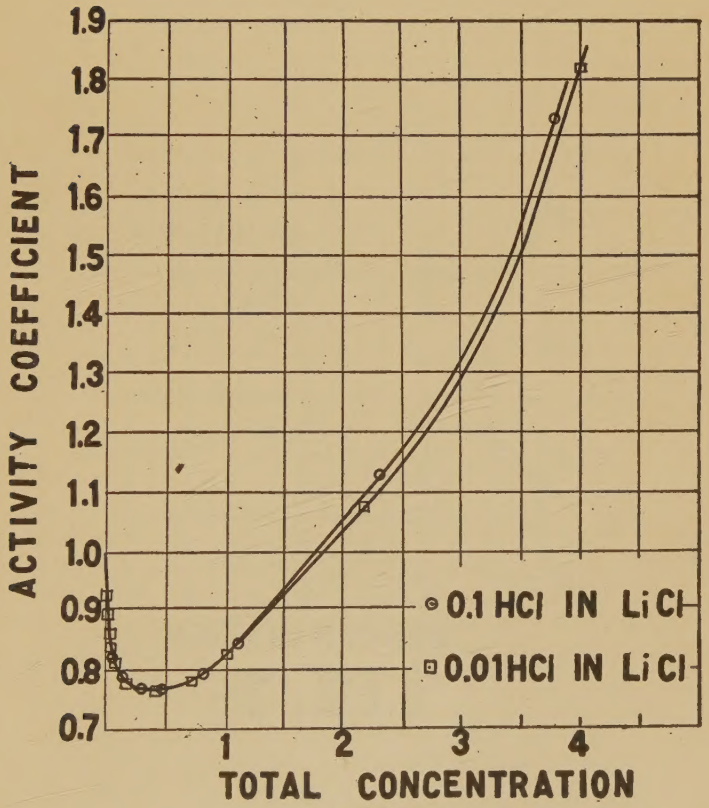
ACTIVITY COEFFICIENT
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
1
2
3
4
TOTAL CONCENTRATION
0.1 HCl IN LiCl
0.01HCl IN LiCl

FIG. 2

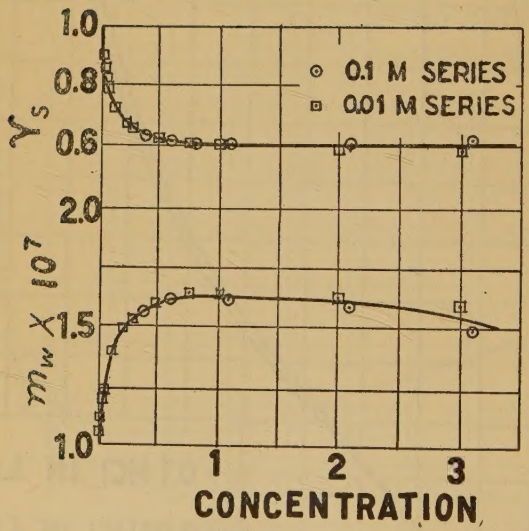
1.0
0.8
0.6
γ_s
2.0
1.5
1.0
$m_w \times 10^7$
0.1 M SERIES
0.01 M SERIES
1
2
3
CONCENTRATION

FIG. 3

PRINTED BY
WESTBROOK PUBLISHING CO.
PHILADELPHIA